JC14 Rec'd PCT/PTO 05 DEC 2001

FORM PTO-1390 (REV. 9-2001) U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NUMBER	
Mo-6840/LeA 33,726	
U S APPLICATION NO (If known, see 37 CFR 1 5)	
To Be Assigned 10/009746	
INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE
PCT/EP00/04968	31 May 2000 (31.05.00)
PRIORITY DATE CLAIMED	
07 June 1999 (7.06.99)	

TITLE OF INVENTION
USE OF Cu-PHTHALOCYANINE SULFONAMIDES AS A DYE FOR WRITE-ONCE OPTICAL DATA STORAGE MEANS

APPLICANT(S) FOR DO/EO/US BRUDER, Friedrich-Karl; RICHTER, Rolf; HAESE, Wilfried; STAWITZ, Josef-Walter; VESPER, Reiner and BERNETH, Horst

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. [X] This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. [X] The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. [X] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. [X] is attached hereto (required only if not communicated by the International Bureau).
   b. [ ] has been communicated by the International Bureau.
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [X] An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. [X] is attached hereto.
   b. [ ] has been previously submitted under 35 U.S.C. 154(d)(4).
7. [ ] Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. [ ] are attached hereto (required only if not communicated by the International Bureau).
   b. [ ] have been communicated by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [ ] have not been made and will not be made.
8. [ ] An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. [ ] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [ ] An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. [ ] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [X] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [X] A FIRST preliminary amendment.
14. [ ] A SECOND or SUBSEQUENT preliminary amendment.
15. [ ] A substitute specification.
16. [ ] A change of power of attorney and/or address letter.
17. [ ] A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. [ ] A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. [ ] A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. [X] Other items or information:

PTO FORM 1449 w/references listed thereon

10/009746

APPLICATION NO (if known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER
To be Assigned	PCT/EP00/04968	Mo-6840/LeA 33,726

21. [X] The following fees are submitted:

531 Rec'd PCT/PTO 05 DEC 200

	CALCULATIONS PTO USE ONLY
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):	
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO **$1040.00**	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO **$890.00**	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **$740.00**	
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$710.00**	
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) **$100.00**	
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 890.00
Surcharge of **$130.00** for furnishing the oath or declaration later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).	$

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	8 - 20 =	0	x **$18.00**	$ 0.00
Independent claims	1 - 3 =	0	x **$84.00**	$ 0.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ **$280.00**	$ 0.00
TOTAL OF ABOVE CALCULATIONS =				$ 890.00
[ ] Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.			+	$ 0.00
SUBTOTAL =				$ 890.00
Processing fee of **$130.00** for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				$
TOTAL NATIONAL FEE =				$
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property +				$ 40.00
TOTAL FEES ENCLOSED =				$ 930.00
			Amount to be refunded:	$
			charged:	$

a. [ ] A check in the amount of $ _____ to cover the above fees is enclosed.

b. [X] Please charge my Deposit Account No. 13-3848 in the amount of $ $930.00 to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 13-3848. A duplicate copy of this sheet is enclosed.

d. [ ] Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO

Aron Preis
Bayer Corporation
Patent Department
100 Bayer Road
Pittsburgh, PA 15205-9741

PATENT TRADEMARK OFFICE 00157

SIGNATURE

Aron Preis
NAME

29,426
REGISTRATION NUMBER

10/009746
531 Rec'd PCT/PTO 05 DEC 2001

PATENT APPLICATION
Mo-6840
LeA 33,726

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF	)
	) PCT/EP00/04968
FRIEDRICH-KARL BRUDER ET AL	)
	)
SERIAL NUMBER: TO BE ASSIGNED	)
	)
FILED: HEREWITH	)
	)
TITLE: USE OF Cu-PHTHALOCYANINE SULFONAMIDES AS A DYE FOR WRITE-ONCE OPTICAL DATA STORAGE MEANS	)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231
Sir:

This preliminary amendment is being filed concurrently with the subject patent application. Upon granting a Serial Number and filing date, please amend the subject patent application as follows.

"Express Mail" mailing label number ET700177007US
Date of Deposit December 5, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, ~~Washington, D.C. 20231~~ Arlington, VA 22202

Donna J. Veatch
(Name of person mailing paper or fee)

(Signature of person mailing paper or fee)

IN THE ABSTRACT:

Please add the following on a separate page.

--USE OF CU-PHTHALOCYANINE SULFONAMIDES AS DYE FOR WRITE-ONCE OPTICAL DATA STORAGE MEANS

ABSTRACT OF THE DISCLOSURE

A write-once optical data carrier is disclosed. The carrier includes a transparent substrate, a writable information layer applied to a surface of the substrate and an optional reflection layer. The writable information layer contains a Cu-phthalocyanine sulfonamide dye represented by the following formula I.

$$\mathbf{CuPc} \begin{cases} (SO_2\text{-}NH\text{-}A\text{-}NR^1R^2)_x \\ (SO_3H)_y \end{cases} \qquad \text{formula I}$$

--

An abstract is included herewith on a separate sheet.

IN THE SPECIFICATION:

Please replace the title at lines 1 and 2 on page 1 of the specification with the following.

--USE OF CU-PHTHALOCYANINE SULFONAMIDES AS DYE FOR WRITE-ONCE OPTICAL DATA STORAGE MEANS--

IN THE CLAIMS:

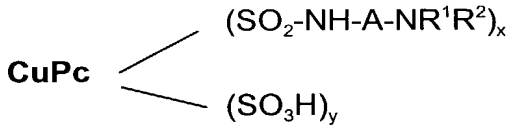
Please cancel Claims 1 and 3-7 without prejudice.

Please replace Claim 2 with the following.

2. (Once Amended, Clean) The optical data carrier of Claim 8 wherein mixtures of phthalocyanine dyes represented by general formula (I) are present in the writable information layer.

Please add the following Claims 8-14.

--8. An optical data carrier comprising a transparent substrate, a writable information layer applied to a surface of said substrate and an optional reflection layer, said writable information layer containing at least one phthalocyanine dye of the general formula I,



formula I

in which

CuPc represents a copper phthalocyanine group,

A represents an optionally substituted straight chain or branched C_2-C_6 alkylene,

R^1 and R^2, independently represent a member selected from the group consisting of hydrogen, straight chain or branched C_1-C_6 alkylene, substituted C_1-C_6 hydroxyalkyl, and an unsubstituted C_1-C_6 alkyl group, or R^1 and R^2, together with the nitrogen atom to which they are bonded denote a heterocyclic 5- or 6-membered ring , optionally containing another heteroatom

x is 2.0 to 4.0,

y is 0 to 1.5 and

and the sum of x and y is 2.0 to 4.0.

9. A process for producing the optical data carrier of Claim 8 comprising applying to a surface of a transparent substrate a solvent mixture containing a phthalocyanine dye of the general formula I to form a writable information layer.

10. The process according to Claim 9 wherein the solvent mixture contains a member selected from the group consisting of benzyl alcohol, water acidified with acetic acid and fluorinated alcohol.

11. The process according to Claim 10 wherein the fluorinated alcohol is 2,2,3,3-tetrafluoropropanol.

12. The process of Claim 9 wherein said solvent mixture is prepared by,

(a) first dissolving the dye in a solvent selected from the group consisting of benzyl alcohol, water acidified with acetic acid and fluorinated alcohol to form a solution; and

(b) then diluting the solution with a member selected from the group consisting of alcohols, ethers, hydrocarbons, halogenated hydrocarbons, CELLOSOLVE ethylene glycol alkyl ethers and ketones.

13. The process of Claim 12 wherein the fluorinated alcohol of step (a) is 2,2,3,3-tetrafluoropropanol; the alcohol of step (b) is selected from at least one of methanol, ethanol, propanol, diacetone alcohol and 1-methyl-2-propanol; the hydrocarbons of step (b) are selected from at least one of hexane, cyclohexane, ethylcyclohexane and octane; the halogentated hydrocarbons of step (b) are selected from at least one of tetrachloroethane and dichloromethane; the ethers of step (b) are selected from at least one of diethyl ether, dipropyl ether and dibutyl ether; the CELLOSOLVE ethylene glycol alkyl ethers of step (b) are selected from at least one of ethylene glycol methyl ether and ethylene glycol ethyl ether; and the ketones of

step (b) are selected from at least one of methylethyl ketone and 4-hydroxy-4-methyl-2-pentanone.

14. The process of Claim 9 wherein the writable information layer is applied by spin-coating.--

REMARKS

Claims in the case are 2 and 8-14 upon entry of this amendment. Claims 1 and 3-7 have been cancelled, Claim 2 has been amended, and Claims 8-14 have been added herein. Claim 2 has been amended to change its dependency from cancelled Claim 1 to added Claim 8.

The title of the specification has been changed to correspond with that of the related International Patent Application No. PCT/EP00/04968, and International Patent Publication No. WO 00/75922 A1. A separate page containing an Abstract of the Disclosure is enclosed herewith.

The present amendment seeks to place the application in better conformance with U.S. practice. Entry of this Preliminary Amendment is respectfully requested.

Respectfully submitted,

By _____

Aron Preis
Attorney for Applicants
Reg. No. 29,426

Bayer Corporation
100 Bayer Road
Pittsburgh, Pennsylvania 15205-9741
(412) 777-8343
FACSIMILE PHONE NUMBER:
(412) 777-8363

s:/sr/jrf0107

10/007746
531 Rec'd PCT/... 05 DEC 2001

VERSIONS WITH MARKINGS TO SHOW CHANGES MADE

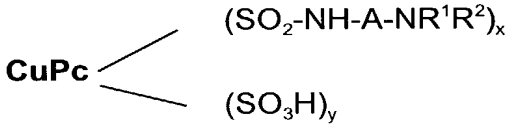
IN THE ABSTRACT:

The following abstract is included herewith on a separate page.

USE OF CU-PHTHALOCYANINE SULFONAMIDES AS DYE FOR WRITE-ONCE OPTICAL DATA STORAGE MEANS

ABSTRACT OF THE DISCLOSURE

A write-once optical data carrier is disclosed. The carrier includes a transparent substrate, a writable information layer applied to a surface of the substrate and an optional reflection layer. The writable information layer contains a Cu-phthalocyanine sulfonamide dye represented by the following formula I.



formula I

IN THE SPECIFICATION:

The title at lines 1 and 2 on page 1 of the specification has been amended as follows.

[Use of Cu phthalocyanine sulfonamides as dyes for write-once optical data stores]

USE OF CU-PHTHALOCYANINE SULFONAMIDES AS DYE FOR WRITE-ONCE OPTICAL DATA STORAGE MEANS

IN THE CLAIMS:

1. (Cancelled)

2. (Once Amended, Marked-Up) [An] The optical data carrier of [according to] Claim 8 [1, characterised in that] wherein mixtures of phthalocyanine dyes represented by [of the] general formula (I) are present in the writable information layer.

3. (Cancelled)

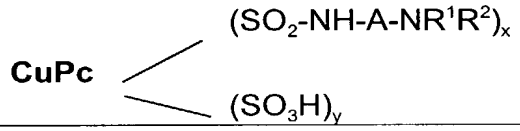
4. (Cancelled)

5. (Cancelled)

6. (Cancelled)

7. (Cancelled)

8. (Added) An optical data carrier comprising a transparent substrate, a writable information layer applied to a surface of said substrate and an optional reflection layer, said writable information layer containing at least one phthalocyanine dye of the general formula I,



formula I

in which

CuPc represents a copper phthalocyanine group,

A represents an optionally substituted straight chain or branched C_2-C_6 alkylene,

R^1 and R^2, independently represent a member selected from the group consisting of hydrogen, straight chain or branched C_1-C_6 alkylene, substituted C_1-C_6 hydroxyalkyl, and an unsubstituted C_1-C_6 alkyl group, or R^1 and R^2, together with the nitrogen atom to which they are bonded denote a heterocyclic 5- or 6-membered ring , optionally containing another heteroatom

x is 2.0 to 4.0,

y is 0 to 1.5 and

and the sum of x and y is 2.0 to 4.0.

9. (Added) A process for producing the optical data carrier of Claim 8 comprising applying to a surface of a transparent substrate a solvent mixture containing a phthalocyanine dye of the general formula I to form a writable information layer.

10. (Added) The process according to Claim 9 wherein the solvent mixture contains a member selected from the group consisting of benzyl alcohol, water acidified with acetic acid and fluorinated alcohol.

11. (Added) The process according to Claim 10 wherein the fluorinated alcohol is 2,2,3,3-tetrafluoropropanol.

12. (Added) The process of Claim 9 wherein said solvent mixture is prepared by,

(a) first dissolving the dye in a solvent selected from the group consisting of benzyl alcohol, water acidified with acetic acid and fluorinated alcohol to form a solution; and

(b) then diluting the solution with a member selected from the group consisting of alcohols, ethers, hydrocarbons, halogenated hydrocarbons, CELLOSOLVE ethylene glycol alkyl ethers and ketones.

13. (Added) The process of Claim 12 wherein the fluorinated alcohol of step (a) is 2,2,3,3-tetrafluoropropanol; the alcohol of step (b) is selected from at least one of methanol, ethanol, propanol, diacetone alcohol and 1-methyl-2-propanol; the hydrocarbons of step (b) are selected from at least one of hexane, cyclohexane, ethylcyclohexane and octane; the halogentated hydrocarbons of step (b) are selected from at least one of tetrachloroethane and dichloromethane; the ethers of step (b) are selected from at least one of diethyl ether, dipropyl ether and dibutyl ether; the CELLOSOLVE ethylene glycol alkyl ethers of step (b) are selected from at

10604746 .120501

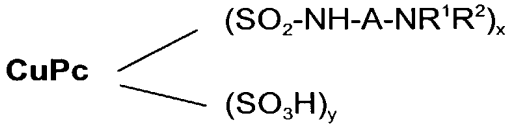
least one of ethylene glycol methyl ether and ethylene glycol ethyl ether; and the ketones of step (b) are selected from at least one of methylethyl ketone and 4-hydroxy-4-methyl-2-pentanone.

14. (Added) The process of Claim 9 wherein the writable information layer is applied by spin-coating.

USE OF CU-PHTHALOCYANINE SULFONAMIDES AS DYE FOR WRITE-ONCE OPTICAL DATA STORAGE MEANS

ABSTRACT OF THE DISCLOSURE

A write-once optical data carrier is disclosed. The carrier includes a transparent substrate, a writable information layer applied to a surface of the substrate and an optional reflection layer. The writable information layer contains a Cu-phthalocyanine sulfonamide dye represented by the following formula I.



formula I

10/019746
531 Rec'd PCT/ 05 DEC 2001

Use of Cu phthalocyanine sulfonamides as dyes for write-once optical data stores

The present invention provides a write-once optical data carrier using Cu phthalocyanine sulfonamides as dyes, in particular for CD-Rs, and also application of the dyes mentioned above to a polymer substrate (in particular polycarbonate) by spin-coating.

Write-once compact disks (CD-Rs) have recently experienced enormous volume growth accompanied by a simultaneous drop in price. The main component in the manufacturing cost is the information-carrying dye. The prior art comprises the use of expensive cyanine, phthalocyanine and azo dye systems which are synthesised specifically for the spectral requirements and the solubility required.

In the patent literature, the necessity for using such expensive modified phthalocyanine dyes is based e.g. on the following arguments:

- Specific substituents prevent the formation of dye associates in thin films. Associates adversely alter the absorption spectrum for applications as optical data stores (US 5124067).
- Specific substituents prevent crystallisation of the dyes in thin films. Crystallites adversely alter the layer homogeneity for application as optical data stores (EP-A2-519419).

Only specific substituents enable solubility of the generally sparingly soluble phthalocyanines in those solvents which do not interfere with the groove structure of the injection moulded plastic substrate when spin-coating on a plastics substrate (mainly polycarbonate) (US 5124067).

Central atoms with a large atomic radius (Pd, Pt, Rh, Ru, In, VO) have to be used in order to achieve the highest possible refractive index at the write and read wavelengths (780 - 820 nm), which guarantees a high signal modulation for application as CD-Rs (EP-A1-0513370).

"Express Mail" mailing label number EV001177007US
Date of Deposit December 5, 2001
I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231 Arlington, VA 22202
Donna J. Veatch
(Name of person mailing paper or fee)
(Signature of person mailing paper or fee)

- Specific substituents and central atoms enable a high molar absorption (>200000). This high molar absorption is required for sufficiently high modulation of the read signal for the CD-R specification (US 5124067).
- Patent EP-A1-519395 (Eastman Kodak Co.) describes metal phthalocyanine dyes with certain sulfonamide groups ($SO_2NR^1R^2$) for write-once optical data stores.
- Patent JP-A-05177946 (Taiyo Yuden) describes certain sulfonamide derivatives of a zinc phthalocyanine dye as the information layer for optical data stores. The dye is intended to be soluble in alcohol and Cellosolve.

These types of highly specialised dye systems are expensive and therefore prevent the cost-effective production of e.g. write-once compact discs (CD-Rs).

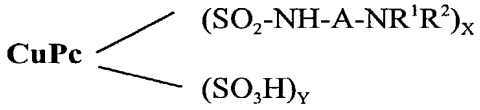
Accordingly, the object of the invention is the provision of a simple to synthesise phthalocyanine dye which complies with the high requirements (such as light stability, favourable signal-to-noise ratio, application to a substrate material without causing damage, etc.) for use as the information layer in a write-once optical data carrier (primarily a CD-R). This would mean that this dye could be prepared much more cheaply and would therefore enable more cost-effective production.

Therefore the invention provides a write-once optical data carrier containing a transparent plastics substrate to the surface of which is applied a writable information layer and optionally a reflection layer, characterised in that at least one phthalocyanine dye of the general formula I is present in the writable information layer.

The invention also provides a process for producing a moulded part consisting of a transparent substrate to the surface of which is applied a writable information layer containing a dye, wherein the dye contains a phthalocyanine dye of the general formula I and is worked up using a solvent mixture.

The invention also provides use of the phthalocyanine dye of the formula I, in particular sulfonamide group-containing copper phthalocyanine dyes of the formula I, in optical data carriers.

The phthalocyanine dye according to the invention can be represented by the formula (I) given below:



formula I

in which

CuPc represents a copper phthalocyanine group,

A represents an optionally substituted straight chain or branched C_2-C_6 alkylene such as e.g. ethylene, propylene, butylene, pentylene, hexylene,

R^1 and R^2, independently, represent hydrogen or each optionally represent a substituted straight chain or branched C_1-C_6 alkylene such as e.g. methylene, ethylene, propylene, butylene, pentylene, hexylene, in particular a substituted C_1-C_6 hydroxyalkyl group as well as an unsubstituted C_1-C_6 alkyl group, or R^1 and R^2, together with the nitrogen atom to which they are bonded, form a heterocyclic 5- or 6-membered ring which optionally contains another heteroatom, e.g. S, N or O,

x is 2.0 to 4.0,

y is 0 to 1.5 and

the sum of x and y is 2.0 to 4.0, preferably 2.5 to 4.0.

Mixtures of the dyes mentioned above may also be used.

Production of the write-once optical data carrier according to the invention is achieved by spin-coating the dye itself or the dye in combination with other dyes or with suitable solvents onto a transparent substrate. For coating purposes, the dye, with or without additives, is dissolved in a suitable solvent or solvent mixture in such a way that the dye constitutes 100 or fewer parts by weight to 100 parts by weight of solvent. Then this primary dye solution can be diluted with a further suitable solvent in such a way that the dye constitutes 20 or fewer parts by weight to 100 parts by weight of solvent. The writable information layer is then metallised under reduced pressure, by sputtering or vapour deposition, and then provided with a protective lacquer.

The substrates may be produced from optically transparent plastics which, if required, have been subjected to surface treatment. Preferred plastics are polycarbonates and polyacrylates, as well as polycycloolefins.

Solvents and solvent mixtures for use when applying a coating of the dye are chosen, on the one hand, for their ability to dissolve the dye and, on the other hand, for having a minimal effect on the substrate. Solvents which are good at dissolving dyes according to the invention are e.g. benzyl alcohol, water acidified with acetic acid, or fluorinated alcohols. Suitable solvents which have a small effect on the substrate are alcohols, ethers, hydrocarbons, halogenated hydrocarbons, Cellosolve, ketones. Examples of such solvents are methanol, ethanol, propanol, 2,2,3,3-tetrafluoropropanol, diacetone alcohol, tetrachloroethane, dichloromethane, diethyl ether, dipropyl ether, dibutyl ether, methylcellosolve, ethylcellosolve, 1-methyl-2-propanol, methylethyl ketone, 4-hydroxy-4-methyl-2-pentanone, hexane, cyclohexane, ethylcyclohexane, octane, benzene, toluene, xylene. Preferred solvents are hydrocarbons and alcohols because they exert the smallest effect on the substrate.

Particularly suitable solvent mixtures for dyes according to the invention are those consisting of benzyl alcohol, water acidified with acetic acid or fluorinated alcohols

mixed with the solvents mentioned above. The initial preparation of a solution in benzyl alcohol, water acidified with acetic acid or fluorinated alcohols followed by dilution with one of the solvents mentioned above is particularly preferred.

Suitable additives for the writable information layer are stabilisers, wetting agents, binders, diluents and sensitisers.

The reflection layer may be prepared from any metal or metal alloy which is conventionally used for writable optical data carriers. Suitable metals or metal alloys may be vapour deposited and sputtered and contain e.g. gold, silver, copper and their alloys with each other or with other metals.

The protective lacquer on top of the reflection layer may consist of UV-curing acrylates.

An intermediate layer which protects the reflection layer from oxidation may also be present.

Writable optical data carriers according to the invention may contain pre-written Read Only Memory (ROM) areas, as described in US 4940618 (Taiyo Yuden). The surface of the substrate may contain a separate thermally deformable layer, as described in US 4990388 (Taiyo Yuden).

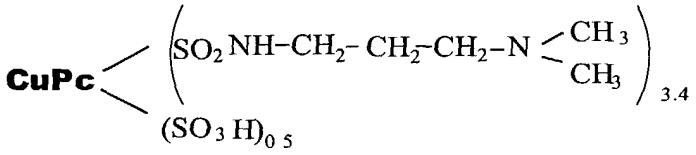
Examples

The following preparative examples illustrate the preparation of dyes according to the invention.

Example 1

138 g copper phthalocyanine are introduced into 700 g chlorosulfonic acid with stirring. The mixture is heated to 136°C - 138°C over 1 hour and held at 136°C - 138°C for 6 hours. The mixture is cooled to 85°C, 130 g of thionyl chloride are allowed to run in at 85°C - 90°C over the course of 2 hours and stirring is then continued for 4 hours at 90°C. After cooling to 20°C - 30°C, the reaction mixture is discharged onto a mixture of 1 l water and 1 kg ice. Furthermore, the temperature is maintained at 0°C by adding ice. The precipitated sulfochloride is filtered off under suction, washed with about 1 l of ice water and dried under suction. The moist filter cake (about 600 g) is introduced into a mixture of 250 ml water and 250 g ice and the pH is adjusted to 7 at 0°C using 10 % strength caustic soda solution. Then 100 g 1-amino-3-dimethylaminopropane are allowed to run in, wherein the pH rises to about 10.5. The mixture is allowed to warm up to 20°C with stirring, the temperature is maintained at 20°C for 1 hour, heated to 40°C and then stirring is continued for 1 hour at 40°C. The pH is maintained at about 10 for the entire time using 10% strength caustic soda solution. The mixture is allowed to cool to room temperature, the pH is adjusted to 8.5 using dilute sulfuric acid, washed with 1 l water in portions and dried under vacuum at 60°C - 80°C.

269 g of dye which corresponds to the approximate formula II when in the form of the free acid are obtained.



formula II

Example 2

138 g copper phthalocyanine are introduced into 560 g chlorosulfonic acid with stirring. The mixture is heated to 110°C - 112°C over 1 hour and held at 110°C - 112°C for 5 hours. The mixture is cooled to 85°C, 85 g of thionyl chloride are allowed to run in at 85°C - 90°C over the course of 2 hours and stirring is then continued for 3 hours at 90°C. After cooling to 20°C - 30°C, the reaction mixture is discharged onto a mixture of 1 l water and 1 kg ice. Furthermore, the temperature is maintained at 0°C by adding ice. The precipitated sulfochloride is filtered off under suction, washed with about 1 l of ice water and dried under suction. The moist filter cake (about 740 g) is introduced into a previously made up mixture of 840 ml ice water and 160 g of 1-amino-3-dimethyl-aminopropane over the course of 1 hour and with cooling. The temperature should then increase and at the end of the introduction procedure is raised first to 40°C and then to 70°C. The temperature is held at 70°C for 1 hour, the product is filtered under suction, washed with 1 l warm water in portions and dried under vacuum at 60°C - 80°C.

252 g of dye which corresponds to the approximate formula III when in the form of the free acid are obtained.

CuPc $\left(SO_2NH-CH_2-CH_2-CH_2-N\begin{matrix}CH_3\\CH_3\end{matrix}\right)_{3\,0}$ formula III

Example 3

138 g copper phthalocyanine are introduced into 500 g chlorosulfonic acid for one hour with stirring. The mixture is heated to 100°C - 102°C over 1 hour and held at 100°C - 102°C for 6 hours. The mixture is cooled to 80°C, 150 g of thionyl chloride are allowed to run in at 80°C over the course of 2 hours and stirring is then continued for 4 hours at 80°C. After cooling to 20°C - 30°C, the reaction mixture is

discharged onto a mixture of 1 l water and 1 kg ice. Furthermore, the temperature is maintained at 0°C by adding ice. The precipitated sulfochloride is filtered off under suction, washed with about 1 l of ice water and dried under suction. The moist filter cake (about 600 g) is introduced into a previously made up mixture of 700 ml ice water and 160 g N-methyl-N-(3-aminopropyl)-ethanolamine over the course of 1 hour with cooling. The temperature should then increase and at the end of the introduction procedure is raised first to 40°C and then to 70°C. The temperature is held at 70°C for 1 hour, the product is filtered under suction, washed with 1 l warm water in portions and dried under vacuum at 60°C - 80°C.

256 g of dye which corresponds to the approximate formula IV when in the form of the free acid are obtained.

CuPc $\left(SO_2NH-CH_2-CH_2-CH_2-N\begin{matrix}CH_3\\ CH_2-CH_2-OH\end{matrix}\right)_{2.5}$ formula IV

The substituents guarantee a solubility of more than 50% in benzyl alcohol, and high solubility in water acidified with acetic acid.

The following examples explain the invention in more detail.

Example 4

A 37.5% solution of the dye in benzyl alcohol was prepared at room temperature. This stock solution was diluted with diacetone alcohol to give a 7.5% dye solution. This solution was applied to a pregrooved polycarbonate substrate by means of spin-coating. The pregrooved polycarbonate was produced as a disk by means of injection moulding. The dimensions of the disk and the groove structure corresponded to those which are normally used for CD-Rs. 100 nm of gold was vapour deposited

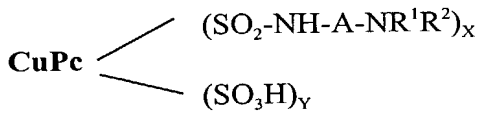
onto the disk with the dye layer as an information carrier. Then a UV-curing acrylic lacquer was applied by means of spin-coating and cured with a UV lamp. Using a commercial test writer for CD-Rs (Pulstec OMT 2000 x 4), e.g. at 12 mW writing power and a 1x write speed (1.4 m/s), a modulation height of 47% (30 % to 70% is the CD-R specification) was obtained for the 3T signal and 69% (>60% is the CD-R specification) was obtained for the 11T signal when reading the information. The reflectivity in the grooves and on the flat sections was 72% and 75% respectively before writing. The specification for CD-Rs requires >65%. The molar absorption of the dye, measured in benzyl alcohol, was about 100 000 l/(mol cm) with a λ_{max} at 690 nm and is thus much lower than the molar absorption of > 200 000 l/(mol cm) cited in US 5124067, which should be desirable for a dye for optical data storage.

Example 5

A 37.5% solution of the dye in benzyl alcohol was prepared at room temperature. This stock solution was diluted with diacetone alcohol to give a 7.5% dye solution. This solution was applied to a pregrooved polycarbonate substrate by means of spin-coating. The pregrooved polycarbonate was produced as a disk by means of injection moulding. The dimensions of the disk and the groove structure corresponded to those which are normally used for CD-Rs. 100 nm of silver was vapour deposited onto the disk with the dye layer as an information carrier. Then a UV-curing acrylic lacquer was applied by means of spin-coating and cured with a UV lamp. Using a commercial test writer for CD-Rs (Pulstec OMT 2000 x 4), e.g. at 15 mW writing power and 2x write speed (2.8 m/s), a modulation height of 41% (30 % to 70% is the CD-R specification) was obtained for the 3T signal and 71% (>60% is the CD-R specification) was obtained for the 11T signal when reading the information. The reflectivity in the grooves and on the flat sections was 72% and 75% respectively before writing. The specification for CD-Rs requires >65%. The molar absorption of the dye, measured in benzyl alcohol, was about 100 000 l/(mol cm) with a λ_{max} at 690 nm and is thus much lower than the molar absorption of > 200 000 l/(mol cm) cited in US 5124067, which should be desirable for a dye for optical data storage.

Claims

1. An optical data carrier containing a transparent substrate to the surface of which is applied a writable information layer and optionally a reflection layer, characterised in that the writable information layer contains at least one phthalocyanine dye of the general formula I,



formula I

in which

CuPc represents a copper phthalocyanine group,

A represents an optionally substituted straight chain or branched C_2-C_6 alkylene,

R^1 and R^2, independently, represent hydrogen or each optionally represent a substituted straight chain or branched C_1-C_6 alkylene, in particular a substituted C_1-C_6 hydroxyalkyl group as well as an unsubstituted C_1-C_6 alkyl group,
or R^1 and R^2, together with the nitrogen atom to which they are bonded, form a heterocyclic 5- or 6-membered ring which optionally contains another heteroatom, e.g. S, N or O,

x is 2.0 to 4.0,

y is 0 to 1.5 and

the sum of x and y is 2.0 to 4.0.

2. An optical data carrier according to Claim 1, characterised in that mixtures of phthalocyanine dyes of the general formula (I) are present in the writable information layer.

3. A process for producing a moulded part consisting of a transparent substrate to the surface of which is applied a writable information layer containing a dye, characterised in that the dye contains a phthalocyanine dye of the general formula I and is worked up using a solvent mixture.

4. A process according to Claim 2, characterised in that one component K1 in the solvent mixture is chosen from the group benzyl alcohol, water acidified with acetic acid or fluorinated alcohols, preferably 2,2,3,3-tetrafluoropropanol.

5. A process according to Claim 3, characterised in that in a first step the dye is dissolved in component K1 and in a second step this solution is diluted with another component K2 which is chosen from the group formed by alcohols, ethers, hydrocarbons, halogenated hydrocarbons, Cellosolve, ketones, preferably chosen from the group formed by methanol, ethanol, propanol, 2,2,3,3-tetrafluoropropanol, diacetone alcohol, tetrachloroethane, dichloromethane, diethyl ether, dipropyl ether, dibutyl ether, methylcellosolve, ethylcellosolve, 1-methyl-2-propanol, methylethyl ketone, 4-hydroxy-4-methyl-2-pentanone, hexane, cyclohexane, ethylcyclohexane, octane, benzene, toluene, xylene.

6. A process according to one of Claims 2 to 4, characterised in that the information layer which contains the dye is applied by spin-coating.

7. Use of sulfonamide group-containing copper phthalocyanine dyes of the formula I for optical data storage.

(12) NACH DEM V[illegible]AG ÜBER DIE INTERNATIONALE ZUSA[illegible]NARBEIT AUF DEM GEBIET DES PATEN[illegible]SENS (PCT) VERÖFFENTLICHTE INTER[illegible]ONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum
Internationales Büro

(43) Internationales Veröffentlichungsdatum
14. Dezember 2000 (14.12.2000)

PCT

(10) Internationale Veröffentlichungsnummer
WO 00/75922 A1

(51) Internationale Patentklassifikation[7]: G11B 7/24, C09B 47/24, B41M 5/26, C09B 47/26

(21) Internationales Aktenzeichen: PCT/EP00/04968

(22) Internationales Anmeldedatum: 31. Mai 2000 (31.05.2000)

(25) Einreichungssprache: Deutsch

(26) Veröffentlichungssprache: Deutsch

(30) Angaben zur Priorität:
199 25 712.4 7. Juni 1999 (07.06.1999) DE

(71) Anmelder (*für alle Bestimmungsstaaten mit Ausnahme von US*): BAYER AKTIENGESELLSCHAFT [DE/DE]; D-51368 Leverkusen (DE).

(72) Erfinder; und
(75) Erfinder/Anmelder (*nur für US*): BRUDER, Friedrich-Karl [DE/DE]; Bodelschwinghstrasse 20, D-47800 Krefeld (DE). RICHTER, Rolf [DE/DE]; Heymannstrasse 67, D-51373 Leverkusen (DE). HAESE, Wilfried [DE/DE]; Osenauerstrasse 32, D-51519 Odenthal (DE). STAWITZ, Josef-Walter [DE/DE]; Am Hagen 1, D-51519 Odenthal (DE). VESPER, Reiner [DE/DE]; Am Gemeindeberg 13, D-42799 Leichlingen (DE). BERNETH, Horst [DE/DE]; Erfurterstrasse 1, D-51373 Leverkusen (DE).

(74) Gemeinsamer Vertreter: BAYER AKTIENGESELLSCHAFT; D-51368 Leverkusen (DE).

(81) Bestimmungsstaaten (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Bestimmungsstaaten (*regional*): ARIPO-Patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), eurasisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI-Patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Veröffentlicht:
— *Mit internationalem Recherchenbericht.*
— *Vor Ablauf der für Änderungen der Ansprüche geltenden Frist; Veröffentlichung wird wiederholt, falls Änderungen eintreffen.*

Zur Erklärung der Zweibuchstaben-Codes, und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

(54) Title: USE OF Cu-PHTHALOCYANINE SULFONAMIDES AS A DYE FOR WRITE-ONCE OPTICAL DATA STORAGE MEANS

(54) Bezeichnung: VERWENDUNG VON Cu-PHTHALOCYANINSULFONSÄUREAMIDEN ALS DYE FÜR EINMAL BESCHREIBBARE OPTISCHE DATENSPEICHER

(57) Abstract: The invention relates to a write-once optical data storage means while using Cu-phthalocyanine sulfonamides as a dye, especially for CD-R, and to the application of the above-mentioned dyes onto a polymer substrate (especially polycarbonate) by means of spin coating.

(57) Zusammenfassung: Die vorliegende Erfindung bezieht sich auf einen einmal beschreibbaren optischen Datenträger unter Verwendung von Cu-Phthalocyaninsulfonsäureamiden als Farbstoff, insbesondere für CD-R, sowie die Applikation der oben genannten Farbstoffe auf ein Polymersubstrat (insbesondere Polycarbonat) durch Spin-Coating.

WO 00/75922 A1

Le A 33 726

COMBINED DECLARATION AND POWER OF ATTORNEY	ATTORNEY DOCKET NO

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought
on the invention entitled

USE OF Cu-PHTHALOCYANINE SULFONAMIDES AS A DYE FOR WRITE-ONCE OPTICAL DATA STORAGE MEANS

the specification of which is attached hereto,

or was filed on **May 31, 2000**

as a PCT Application Serial No. **PCT/EP00/04968**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

199 25 712.4	**Germany**	**June 7, 1999**
(Number)	(Country)	(Month/Day/Year Filed)

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occured between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Le A 33 726-US

10609246.120502

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and this application and to transact all business in the Patent and Trademark Office conne

JOSEPH C. GIL, Patent Office Registration Number 26,602 ARON PREIS, Patent Office Registration Number 29,426 LYNDANNE M. WHALEN, Patent Office Registration Number 29,457 THOMAS W. ROY, Patent Office Registration Number 29,582 RICHARD E. L. HENDERSON, Patent Office Registration Number 31,619 GODFRIED R. AKORLI, Patent Office Registration Number 28,779 N. DENISE BROWN, Patent Office Registration Number 36,097 NOLAND J. CHEUNG, Patent Office Registration Number 39,138 DIDERICO VAN EYL, Patent Office Registration Number 38,641 CAROLYN M. SLOANE, Patent Office Registration Number 44,339 JAMES R. FRANKS, Patent Office Registration Number 42,552 JACKIE ANN ZURCHER, Patent Office Registration Number 42,251 RAYMOND J. HARMUTH, Patent Office Registration Number 33,896
all of Bayer Corporation, Pittsburgh, Pennsylvania 15205-9741

Send Correspondence To: **Patent Department** **Bayer Corporation** (412) 777-2349 **100 Bayer Road** **Pittsburgh, Pennsylvania 15205-9741**	

1) FULL NAME OF SOLE OR FIRST INVENTOR: Friedrich-Karl Bruder	INVENTOR'S SIGNATURE	DATE: 5.10.01
RESIDENCE: D 47802 Krefeld, Germany DEX		CITIZENSHIP: German
POST OFFICE ADDRESS: c/o Bayer Aktiengesellschaft, D 51368 Leverkusen, Germany		
2) FULL NAME OF SECOND INVENTOR: Rolf Richter	INVENTOR'S SIGNATURE	DATE: 27.09.01
RESIDENCE: D 51373 Leverkusen, Germany DEX		CITIZENSHIP: German
POST OFFICE ADDRESS: c/o Bayer Aktiengesellschaft, D 51368 Leverkusen, Germany		
3) FULL NAME OF THIRD INVENTOR: Wilfried Haese	INVENTOR'S SIGNATURE	DATE: 1.10.01
RESIDENCE: D 51519 Odenthal, Germany DEX		CITIZENSHIP: German
POST OFFICE ADDRESS: c/o Bayer Aktiengesellschaft, D 51368 Leverkusen, Germany		
4) FULL NAME OF FOURTH INVENTOR: Josef-Walter Stawitz	INVENTOR'S SIGNATURE	DATE: 9.10.01
RESIDENCE: D 51519 Odenthal, Germany DEX		CITIZENSHIP: German
POST OFFICE ADDRESS: c/o Bayer Aktiengesellschaft, D 51368 Leverkusen, Germany		
5) FULL NAME OF FIFTH INVENTOR: Reiner Vesper	INVENTOR'S SIGNATURE	DATE: 10.10.01
RESIDENCE: D 42799 Leichlingen, Germany		CITIZENSHIP: German
POST OFFICE ADDRESS: c/o Bayer Aktiengesellschaft, D 51368 Leverkusen, Germany		
6) FULL NAME OF SIXTH INVENTOR: Horst Berneth	INVENTOR'S SIGNATURE	DATE: 2001-10-08
RESIDENCE: D 51373 Leverkusen, Germany DEX		CITIZENSHIP: German
POST OFFICE ADDRESS: c/o Bayer Aktiengesellschaft, D 51368 Leverkusen, Germany		
FULL NAME OF SEVENTH INVENTOR	INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP
POST OFFICE ADDRESS		